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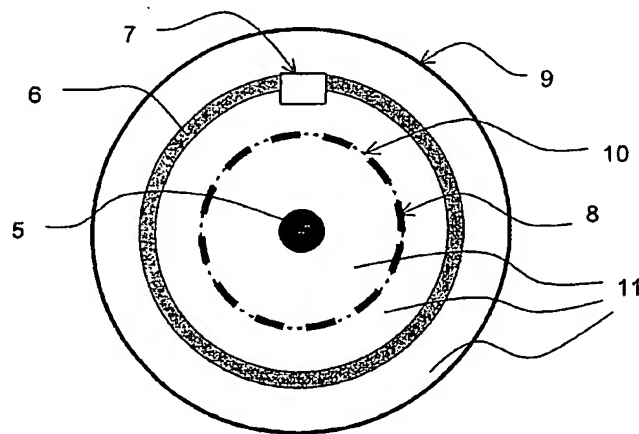
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(54) Title: REMOVING SURFACE OXIDES FROM COPPER



(57) Abstract: The invention relates to a method for improving the quality of an object made of a copper-based metal alloy, according to which method the object is treated at least in an oxide removal unit (3), so that in the oxide removal unit, oxides are removed from the object surface by means of cathodic reduction. The invention also relates to an arrangement for realizing the method according to claim 1 in order to improve the quality of an object made of a copper-based metal alloy, said arrangement comprising at least an oxide removal unit. Which arrangement includes elements for realizing a cathodic reduction, such as an anode (6), a cathode (5) and an electrolyte (11), so that the access of the oxygen created on the anode to the cathode is prevented by a membrane (18) that is impermeable to oxygen.

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REMOVING SURFACE OXIDES FROM COPPER

The invention relates to a method and arrangement, defined in the independent claims, for improving the quality of an object made of a copper-based metal alloy.

On the surfaces of objects made of copper or copper alloys, there may be created
5 oxide layers disturbing their further processing, during production, for example
during casting and various annealing treatments. Therefore the surfaces must
often be cleaned of the oxide layers accumulated on the surfaces. Oxide layers
are difficult to observe or measure on the copper surface, and they are not
necessarily distinguished without specific equipment. The removal of thick oxide
10 layers from the copper surface is relatively simple, but on the other hand, the
removal of the last molecular layers has turned out to be more troublesome.
However, even oxide layers that are not apparent for visual estimation are
defective for the quality of the copper product. Oxide layers on the surface of
copper disturb for instance extrusion, so that when removing the oxide layers,
15 there is created harmful extrusion scrap. The treatment and recirculation of
extrusion scrap lead to extra expenses. When copper wire is produced by
extrusion, a completely oxide-free supply wire ensures a better operation, and a
nearly faultless quality is obtained for the products.

In the cleaning of copper metal surfaces, there is generally applied etching, i.e. the
20 metal surface is chemically cleaned of the oxide layer by means of dissolution. It is
generally known that all grease and oil should be removed from the product
surface before etching. Normally the etching of copper metals is carried out in a
sulfuric acid – water solution, and it removes the major part of the oxides created
on the surface. In conventional sulfuric acid etching, there is achieved a low oxide
25 layer level immediately after the etching process, but in practice the dissolved
oxygen of the acid and the slowness of the final washing may double the oxide
layer after drying.

Mechanical procedures, such as surface peeling or grinding may damage the
surface of the object to be cleaned, and they are not necessarily suited in a
30 surface cleaning process that requires precision.

One way of preventing the creation of oxides on the surface of a copper object is to insulate the copper object by a protective gas atmosphere in order to prevent oxidation.

From the publication WO 02/32595 there is known a mechanism, according to which from the surface of an aluminum or copper object, the surface layer is scraped off mechanically, so that impurities, such as oxide layers, occurring on the surface can be eliminated. However, the mechanical cleaning of the surface may result in remarkable material losses with respect to the aluminum or copper proper. In addition, the material surface may be damaged by mechanical scraping.

10 The recovery and further processing of the scraped surface layers also cause extra trouble.

The object of the present invention is to avoid the drawbacks of the prior art and to introduce a new solution for improving the quality of an object made of a copper-based metal alloy. A particular object of the invention is to improve the quality of an object made of a copper-based metal alloy by removing oxides from the surface thereof by means of cathodic reduction.

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The invention is characterized by what is set forth in the characterizing part of the independent claims. Other preferred embodiments of the invention are characterized by what is set forth in the other claims.

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The method according to the invention has many advantages. The invention relates to a method for improving the quality of an object made of a copper-based metal alloy, according to which method the object is treated at least in an oxide removal unit, so that in the oxide removal unit, oxides are removed from the object surface by means of cathodic reduction. By applying cathodic reduction, the oxides present on the copper surface are reduced to copper, so that the oxide layer is eliminated from the surface of the copper object. According to a preferred embodiment of the invention, the employed electrolyte in cathodic reduction is sodium carbonate solution. According to another preferred embodiment of the invention, the employed electrolyte in cathodic reduction is sulfuric acid solution.

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According to a preferred embodiment of the invention, the employed cathode in cathodic reduction is the object made of a copper-based metal alloy, and the employed anode is a non-soluble material, such as a platinum anode or a platinum-coated titanium anode. Other suitable anode materials are for example lead or titanium coated with iridium oxide. In cathodic reduction, on the anode there is created oxygen, and on the cathode there is created copper. In connection with the anode, there is arranged at least one exhaust aperture for enabling the exhaustion of oxygen. According to a preferred embodiment of the invention, in cathodic reduction there is used an ion-selective membrane that is impermeable to oxygen. The membrane is advantageously placed between the anode and the cathode in order to prevent the oxygen from being transferred from the anode to the cathode. From the space between the anode and the membrane, oxygen is exhausted along with the solution circulation, or through oxygen exhaustion apertures. According to a preferred embodiment, the membrane is arranged symmetrically around the cathode, so that it surrounds the whole cathode. In this fashion, the oxidation and reduction reactions are made to proceed smoothly, and the voltage is distributed evenly in the whole cell.

According to a preferred embodiment of the invention, an object made of a copper-based metal alloy is subjected to preliminary washing prior to the cathodic reduction. According to another embodiment, an object made of a copper-based metal alloy is subjected to etching by sulfuric acid before the cathodic reduction. Thus the thickest oxide films are removed rapidly prior to the cathodic reduction. When necessary, sulfuric acid films are removed by mechanical drying. According to a preferred embodiment of the invention, the object is subjected to a rapid pressurized water washing after the cathodic reduction.

According to the invention, the remaining oxide layer after a treatment performed in the oxide removal unit is preferably left at a degree of 0.001 – 0.01 nanometers, i.e. advantageously the oxide film is nearly completely removed. According to a preferred embodiment of the invention, the object is after the oxide removal unit conducted into a working process, such as a continuously operated extrusion treatment. The oxide removal unit and the working process are insulated from the surroundings by protective gas.

The invention also relates to an arrangement for realizing the method according to claim 1 for improving the quality of an object made of a copper-based metal alloy, said arrangement comprising at least an oxide removal unit and elements for realizing cathodic reduction, such as an anode, a cathode and an electrolyte, so that the access of the oxygen created on the anode to the cathode is prevented by a membrane that is impermeable to oxygen.

In general, by utilizing the invention, continuously operated extrusion of copper is facilitated and speeded up, and the recovery from the process is improved, when the oxides present on the surface are eliminated. The creation of extrusion scrap is avoided, and the working life of the equipment is extended. The quality of the copper products is made better when the harmful oxide layers are removed.

The invention is described in more detail below with reference to the appended drawings.

Figure 1 A diagram of the principle of the method according to the invention

Figure 2 Cross-section of cathodic reduction

Figure 1 illustrates the method according to the invention in the form of a block diagram. A round wire-like object 1 made of copper is conducted to an oxide removal unit 3. The oxide removal unit 3 includes a cathodic reduction arrangement. The oxide-free copper wire 2 obtained from the oxide removal unit is conducted to a working process, such as a continuously operated extrusion treatment 4. The oxide removal unit and the working process unit are insulated from the surroundings by protective gas.

Figure 2 shows a cross-section of the cathodic reduction process carried out in an oxide removal unit. According to the example, copper wire is washed prior to the oxygen removal proper. Thereafter the copper wire is subjected to preliminary etching by sulfuric acid, so that the thickest oxides layers are removed. Sulfuric acid films left after etching are removed for instance by mechanical drying. Then the cathodic reduction is performed. The copper wire 5 is placed in a chamber 9

containing sodium carbonate solution 11, and electric current is conducted to said chamber. The copper wire 5 serves as a cathode, on which copper oxide is reduced to copper, and thus the oxides are eliminated nearly completely from the copper surface. The employed anode 6 is a non-soluble platinum anode, on which oxygen is created. The solution 11 fills the chamber 9 all over. The access of the oxygen created on the anode is prevented by an ion selective membrane 8 that is impermeable to oxygen, which preferably surrounds the whole cathode. The employed housing for the membrane is an insulated, perforated tube 10 in order to maintain the liquid connection. Advantageously the membrane is symmetrically arranged around the cathode, which helps the reduction and oxidation reactions to proceed evenly. In connection with the anode 6 there is provided an oxygen exhaust aperture 7, through which the oxygen created on the anode is removed from the system.

For a man skilled in the art, it is obvious that the various embodiments of the invention are not restricted to the examples described above, but may vary within the scope of the appended claims.

CLAIMS

1. A method for improving the quality of an object made of a copper-based metal alloy, according to which method the object is treated at least in an oxide removal unit (3), **characterized** in that in the oxide removal unit, oxides are removed from the object surface by means of cathodic reduction.
2. A method according to claim 1, **characterized** in that in cathodic reduction, the employed electrolyte (11) is sodium carbonate solution.
3. A method according to claim 1, **characterized** in that in cathodic reduction, the employed electrolyte (11) is sulfuric acid solution.
4. A method according to claim 1, 2 or 3, **characterized** in that in cathodic reduction, the employed cathode (5) is an object made of a copper-based metal alloy, and the employed anode (6) is a non-soluble material.
5. A method according to claim 4, **characterized** in that the employed anode (6) is a non-soluble material, such as platinum.
6. A method according to any of the preceding claims, **characterized** in that in cathodic reduction, on the anode (6) there is created oxygen and on the cathode (5) there is created copper.
7. A method according to claim 4, 5 or 6, **characterized** in that in connection with the anode (6), there is arranged at least one oxygen exhaust aperture (7) for enabling the exhaustion of oxygen.
8. A method according to any of the preceding claims, **characterized** in that in cathodic reduction, there is used an ion-selective membrane (8) that is impermeable to oxygen.
9. A method according to claim 8, **characterized** in that the membrane is placed between the anode and the cathode in order to prevent the oxygen from proceeding from the anode to the cathode.

10. A method according to claim 8 or 9, **characterized** in that the membrane (8) is arranged symmetrically around the cathode, so that it surrounds the whole cathode (5).
- 5 11. A method according to any of the preceding claims, **characterized** in that an object made of a copper-based metal alloy is subjected to a preliminary washing prior to the cathodic reduction.
12. A method according to any of the preceding claims, **characterized** in that an object made of a copper-based metal alloy is subjected to etching by sulfuric acid prior to the cathodic reduction.
- 10 13. A method according to claim 12, **characterized** in that sulfuric acid films are removed by mechanical drying.
14. A method according to any of the preceding claims, **characterized** in that after cathodic reduction, the object is subjected to a rapid pressurized water washing.
- 15 15. A method according to any of the preceding claims, **characterized** in that after the oxide removal unit (3), the object made of a copper-based metal alloy is conducted into a working process (4), such as a continuously operated extrusion treatment.
- 20 16. A method according to claim 15, **characterized** in that the oxide removal unit (3) and the working process (4) are insulated from the surroundings by protective gas.
- 25 17. An arrangement for realizing the method according to claim 1 for improving the quality of an object made of a copper-based material, said arrangement comprising at least an oxide removal unit, **characterized** in that the arrangement includes elements for realizing a cathodic reduction, such as an anode (6), a cathode (5) and an electrolyte (11), so that the access of the gas created on the anode to the cathode is prevented by a membrane (8) that is impermeable to oxygen.

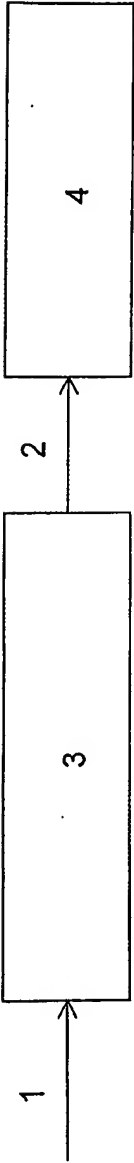


Fig. 1

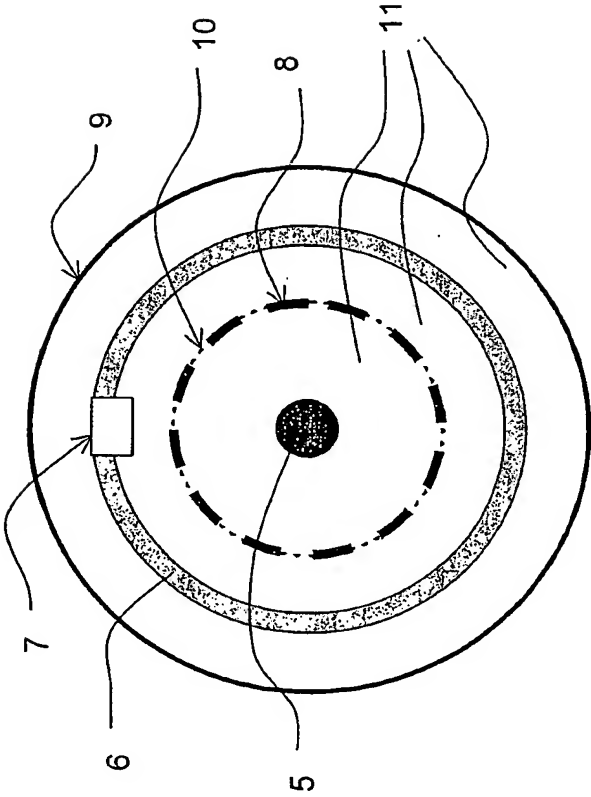


Fig. 2